Nonlinear Oscillation and Multiscale Dynamics in a Closed Chemical Reaction

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History

- G.T. Fechner, et al. (1828-1900)
- A. Lotka (1910-1920).
- V. Volterra (1926)
- B. Belousov (1951)
- A.M. Zhabotinsky (1961)
- Ilya Prigogine and his Brussels school

⋮

BZ reaction–chemical reaction exhibiting oscillatory behavior.

Systems of Chemical Reaction

- Open system
  Exchange of both molecules and energy with the surroundings is allowed. (for *in vivo* studies)
- Closed system
  Exchange of energy but NOT molecules with the surroundings is allowed. (for *in vitro* studies)

Most of currently exisiting reaction models exihiting oscillation are open system.

Irreversible Lotka-Volterra Model

- Irreversible Reaction.

$$A + X \xrightarrow{k_1} 2X, \quad X + Y \xrightarrow{k_2} 2Y, \quad Y \xrightarrow{k_3} B, \tag{1}$$

- By the Law of Mass Action, one has

$$\text{Closed system} \quad \begin{cases} \dot{c}_A &= -k_1 c_A x \\ \dot{x} &= k_1 c_A x - k_2 xy \\ \dot{y} &= k_2 xy - k_3 y \\ \dot{c}_B &= k_3 y. \end{cases} \tag{2}$$

$$\text{Open system} \quad \begin{cases} \dot{x} &= k_1 c_A x - k_2 xy \\ \dot{y} &= k_2 xy - k_3 y. \end{cases} \tag{3}$$

Reversible Lotka-Volterra System

- Reversible Reaction.

$$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X, \qquad X + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Y, \qquad Y \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B. \tag{4}$$

Reversible Lotka-Volterra System

- Reversible Reaction.

$$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X, \qquad X + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Y, \qquad Y \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B. \tag{4}$$

- Rate Equations

$$\begin{cases} \dfrac{dx}{dt} & = & k_1 c_A x - k_{-1}x^2 - k_2 xy + k_{-2}y^2, \\ \dfrac{dy}{dt} & = & k_2 xy - k_{-2}y^2 - k_3 y + k_{-3}c_B, \\ \dfrac{dc_A}{dt} & = & -k_1 c_A x + k_{-1}x^2, \\ \dfrac{dc_B}{dt} & = & k_3 y - k_{-3}c_B. \end{cases} \tag{5}$$

Nondimensionalization

- Rescaling

$$\begin{array}{c} u=\frac{k_2}{k_3}x, \quad v=\frac{k_2}{k_3}y, \ w=\frac{k_1}{k_3}c_A, \ z=\frac{k_2}{k_3}c_B, \ \tau=k_3 t, \\ \sigma=\frac{k_1}{k_2}\ll 1, \ \frac{k_{-1}}{k_1}=\frac{k_{-2}}{k_2}=\frac{k_{-3}}{k_3}=\varepsilon\ll\sigma. \end{array} \tag{6}$$

- Dimensionless Form.

$$\left\{ \begin{array}{lcl} \frac{du}{d\tau} & = & u(w-v)-\varepsilon(\sigma u^2-v^2) \\ \frac{dv}{d\tau} & = & v(u-1)-\varepsilon v^2+\varepsilon z \\ \frac{dw}{d\tau} & = & -\sigma(wu-\varepsilon\sigma u^2). \\ \frac{dz}{d\tau} & = & v-\varepsilon z. \end{array} \right. \tag{7}$$

Closed System

- Linear Conservation Law.

$$u + v + \frac{w}{\sigma} + z = \xi = constant.$$

- Reduced system.

$$\left\{\begin{array}{rcl} \dfrac{du}{d\tau} & = & u(w-v) - \varepsilon(\sigma u^2 - v^2) \\ \dfrac{dv}{d\tau} & = & v(u-1) - \varepsilon v^2 + \varepsilon\left(\xi - u - v - \frac{w}{\sigma}\right) \\ \dfrac{dw}{d\tau} & = & -\sigma(wu - \varepsilon\sigma u^2). \end{array}\right. \tag{8}$$

Closed System

Denote

$$\mathcal{T} = \left\{(u, v, w) \in \mathbb{R}^3, u, v, w > 0, \text{ and } u + v + \frac{w}{\sigma} \leq \xi\right\}.$$

Then $\mathcal{T}$ is positively invariant under the flow induced by the closed system (8), and $\mathcal{T}$ is called the reaction zone.

System (8) has a unique interior equilibrium point $P \in \mathcal{T}$ at which its Jacobian matrix has three real eigenvalues

$$|\lambda_1 + (1 + \varepsilon)| \sim \varepsilon^2, \quad |\lambda_2 + \varepsilon\xi| \sim \varepsilon^2, \quad \left|\lambda_3 + \sigma\varepsilon^2\xi\right| \sim \sigma^2\varepsilon^3.$$

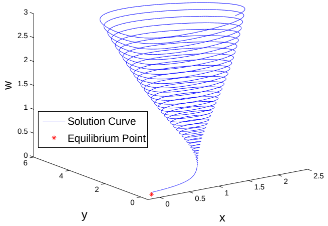
Thus P is an asymptotically stable node.

The Second Law of Thermodynamics

P is the global attractor of system (8) in $\mathcal{T}$. The free energy

$$L = u\ln\left(\frac{u}{u*}\right) + v\ln\left(\frac{v}{v*}\right) + \frac{w}{\sigma}\ln\left(\frac{w}{w*}\right) + \left(\xi - u - v - \frac{w}{\sigma}\right)\ln\left(\frac{\xi - u - v - \frac{w}{\sigma}}{\xi - u^* - v^* - \frac{w^*}{\sigma}}\right)$$

serves as the Lyapunov function, where $P = (u^*, v^*, w^*)$.

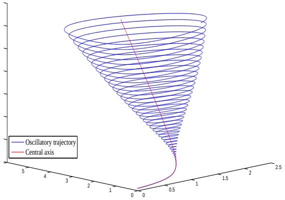


Far-from-equilibrium – Oscillation Zone

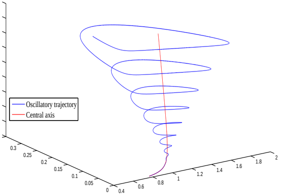
There exist $\mathcal{T}^o \subset \mathcal{T}$ and a 1D curve $W^o_{\sigma,\varepsilon} \subset \mathcal{T}^o$ such that all the oscillatory solutions in $\mathcal{T}^o$ go around $W^o_{\sigma,\varepsilon}$. The total oscillation time is $T_o \sim -\frac{\ln\sigma}{\sigma}$. For fixed $w_0 > w_1$, there are at least N complete oscillations by 2π with w decreasing from w_0 to w_1, where $N \geq \frac{\ln w_0 - \ln w_1}{2\sigma K} - 1$. And $W^o_{\sigma,\varepsilon}$ is approximately given by

$$W^o_{\sigma,\varepsilon} \sim \left\{ (u, v, w), \quad u = \frac{1}{1+\sigma}, \; v = w, w \in [\underline{w}, \bar{w}] \right\}.$$

Large ξ



Small ξ



Existence of $W^o_{\sigma,\varepsilon}$

Consider the partially perturbed system where $\varepsilon = 0$

$$\begin{cases} \dot{u} &= u(w-v) \\ \dot{v} &= v(u-1) \\ \dot{w} &= 0 \end{cases} \Rightarrow \begin{cases} \dot{u} &= u(w-v) \\ \dot{v} &= v(u-1) \\ \dot{w} &= -\sigma w u \end{cases} \tag{9}$$

which admits a stable invariant manifold

$$W^o_\sigma = \left\{ (u,v,w), \quad u = \mu_\sigma = \frac{1}{1+\sigma}, \ v = w \geq 0 \right\}.$$

with Lyapunov function

$$E_\sigma = (1+\sigma)\left[u - \mu_\sigma - \ln\left(\frac{u}{\mu_\sigma}\right)\right] + \left[v - w - w \ln\left(\frac{v}{w}\right)\right]$$

Normal Hyperbolicity of W^0_σ?

- Generalized Lyapunov Type Numbers

$$\begin{aligned} \gamma_L(W^o_\sigma) &= \overline{\lim_{t\to-\infty}} \left\|\pi^N_p D\phi_t(W^o_\sigma)\right\|^{\frac{1}{t}} < 1, \\ \sigma_L(W^o_\sigma) &= \overline{\lim_{t\to-\infty}} \frac{\log\left\|D\phi_t(W^o_\sigma)\pi^T_p\right\|}{\log\left\|\pi^N_p D\phi_t(W^o_\sigma)\right\|} \geq 2, \end{aligned}$$

- Exponential Dichotomy

$$u \to \mu_\sigma + x, \quad v \to v + w, \quad w \to w, \quad X = (x, y)^T$$

$$\begin{cases} \sigma X' = A_\sigma(w)X + G_{\sigma,\varepsilon}(X, w) \\ w' = F_{\sigma,\varepsilon}(X, w), \end{cases} \quad A_\sigma(w) = \begin{bmatrix} 0 & -\mu_\sigma \\ \frac{w}{\mu_\sigma} & -\sigma\mu_\sigma \end{bmatrix} \tag{10}$$

where $Re(\lambda(A_\sigma)) \leq -\frac{\sigma\mu_\sigma}{2}$ as $w \geq \frac{\sigma^2\mu_\sigma^2}{4}$.

Proof–Sakamoto (1990)

- Modified system

$$\begin{cases} \sigma X' = A_\sigma(w)X + G_{\sigma,\varepsilon}(X,w) \\ w' = F_{\sigma,\varepsilon}(X,w)\chi_{[\sigma^2,\sigma\xi]}(w) \end{cases} \tag{11}$$

- $$\begin{cases} X(t) &= \dfrac{1}{\sigma}\displaystyle\int_{-\infty}^{t} \Phi_\sigma(t,s,w(s))G_{\sigma,\varepsilon}(X,w)ds \\ w(t) &= H(\eta,X)(t) < \infty, \qquad w(0) = \eta \in [\sigma^2,\sigma\xi]. \end{cases}$$
- $\mathcal{F}(X) = \dfrac{1}{\sigma}\displaystyle\int_{-\infty}^{t} \Phi_\sigma(t,s,H(\eta,X)(s))G_{\sigma,\varepsilon}(X,H(\eta,X)(s))ds.$
- $\mathcal{F}$ is a contraction as $|X| \le \delta$ for some $\delta \Rightarrow \mathcal{F}(X^*_\eta) = X^*_\eta$.
- $W^o_{\sigma,\varepsilon} = \big\{(u = \mu_\sigma + x^*_w(0), v = w + y^*_w(0), w), w \in [\sigma^2,\sigma\xi]\big\}.$

Closer Look of Oscillatory Behavior

Define

$$\mathcal{T}_1^o = \{(u,v,w) \in \mathcal{T} : w \geq \sigma\}, \ \mathcal{T}_2^o = \left\{(u,v,w) \in \mathcal{T} : w \geq \sigma^2\right\},$$
$$\Omega_- = \{(u,v,w) \in \mathcal{T} : v < w\}, \ \Omega_+ = \{(u,v,w) \in \mathcal{T} : v > w\}.$$

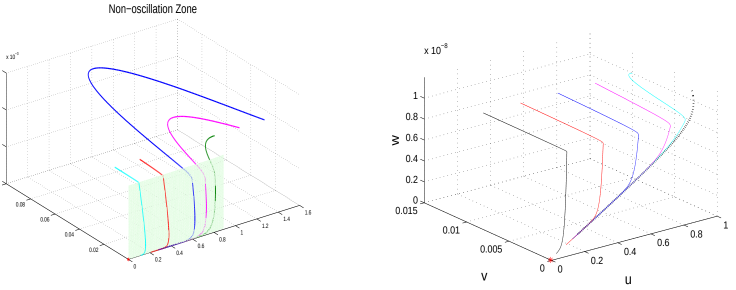
For $\varepsilon \ll \sigma \ll 1$ and some $1 < \alpha < 2$,

- $\mathcal{T}_1^o \subset \mathcal{T}^o \subset \mathcal{T}_2^o$.
- In Ω_+, $\frac{w_{2k+1}}{w_{2k}} \sim 1$ and $\frac{E_{2k+1}}{E_{2k}} \sim 1$.
- In Ω_-, $\frac{w_{2k+2}}{w_{2k+1}} < e^{-\sigma c_1(w_0,E_0)}$ and $\frac{E_{2k+2}}{E_{2k+1}} < e^{-\sigma c_2(w_0,E_0)}$.
- At the bottom of $\mathcal{T}^o$ where $w \sim \sigma^\alpha$, $E \sim (\alpha-2)\sigma^\alpha \ln \sigma$.

Near-equilibrium – Non-oscillation Zone

There exist $\mathcal{T}^n \subset \mathcal{T}$ and a 2D strongly stable invariant manifold $M^n_{\sigma,\varepsilon} \subset \mathcal{T}^n$ and a 1D stable curve $W^n_{\sigma,\varepsilon} \subset M^n_{\sigma,\varepsilon}$. The "total time" in $\mathcal{T}^n$ is $T_n \sim -\frac{\ln \varepsilon}{\varepsilon}$. And

$$W^n_{\sigma,\varepsilon} \sim \left\{(u,v,w), \quad v = \varepsilon\frac{\xi - u}{1-u}, \ w = \sigma\varepsilon u, \ u \in [0,\bar{u}], \bar{u} < 1\right\}.$$



Existence of $M^n_{\sigma,\varepsilon}$

Under the following transformation

$$u \to u, \qquad v \to \varepsilon v, \qquad w \to \sigma\varepsilon w.$$

system (8) becomes

$$\begin{cases} \dfrac{du}{d\tau} &= \varepsilon\left[u(\sigma w - v) - (\sigma u^2 - \varepsilon^2 v^2)\right] \\ \dfrac{dv}{d\tau} &= v(u-1) - \varepsilon^2 v^2 + (\xi - u - \varepsilon v - \varepsilon w) \\ \dfrac{dw}{d\tau} &= -\sigma u(w-u). \end{cases} \tag{12}$$

By Fenichel's Theorem, critical manifold

$$M^n_0 = \left\{(u,v,w), \quad v = \frac{\xi - u}{1-u}, \; u, w \in [0, \bar{u}], \bar{u} < 1\right\}$$

is normally hyperbolic and thus persists under the perturbation.

Existence of $W^n_{\sigma,\varepsilon}$

- Reduced System

$$\begin{cases} \dfrac{du}{d\tau_1} = \dfrac{\varepsilon}{\sigma}\left[u(\sigma w - h_{\sigma,\varepsilon}(u,w)) - (\sigma u^2 - \varepsilon^2 h^2_{\sigma,\varepsilon}(u,w))\right] \\ \dfrac{dw}{d\tau_1} = -u(w-u). \end{cases} \tag{13}$$

Critical manifold

$$W^n_0 = \{(u,w), \quad w = u \in [\underline{u}, \bar{u}], 0 < \underline{u} < \bar{u} < 1\}$$

is normally hyperbolic and thus persists under the perturbation.

In the Vicinity of Equilibrium P

- Stable Invariant manifold may be applied.
- Further Rescaling

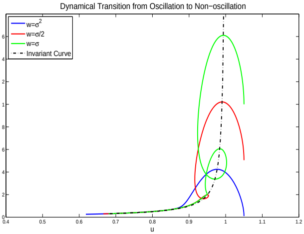
$$u \to \sigma\varepsilon u, \quad v \to v, \quad w \to w, \quad \tau_2 = \frac{\varepsilon}{\sigma}\tau_1.$$

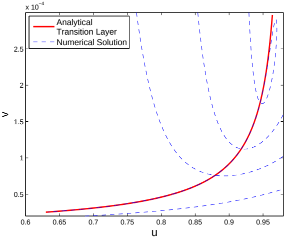
yields

$$\begin{cases} \dfrac{du}{d\tau_2} = u(\sigma w - h_{\sigma,\varepsilon}) - (\sigma^2\varepsilon u^2 - \dfrac{\varepsilon}{\sigma}h_{\sigma,\varepsilon}) \\ \dfrac{dw}{d\tau_2} = -\sigma^2 u(w - \sigma\varepsilon u). \end{cases} \tag{14}$$

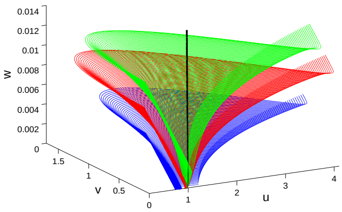
Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$

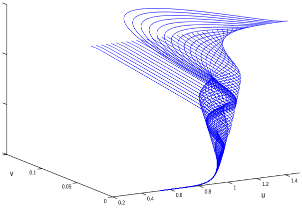
The passage of entering the non-oscillation zone $\mathcal{T}^n$ from the oscillation zone $\mathcal{T}^o$ is around the portion of the central axis connecting $W^o_{\sigma,\varepsilon}$ and $W^n_{\sigma,\varepsilon}$. This is exactly where the transition occurs.





Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$





A General Network of Chemical Reactions

Consider a system of chemical reactions whose rate equations, by the law of mass action, are given by

$$X' = V(X) = AR(X) \tag{15}$$

where $A = (a_{ij})$ is the stoichiometric matrix and $R_i(X) = r_i^f(X) - r_i^b(X)$ with

$$r_i^f(X) = k_i \prod_{a_{ji}<0} x_j^{-a_{ji}}, \quad r_i^b(X) = k_{-i} \prod_{a_{ji}>0} x_j^{a_{ji}}.$$

Rewrite equation (15) as

$$\begin{cases} X_1' = F_1(X_1, X_2) \\ X_2' = F_2(X_1, X_2). \end{cases} \tag{16}$$

Canonical System and Grand Canonical System

- Canonical System.
  By the linear conservation law $M_1X_1 + M_2X_2 = \xi$, equation (16) is reduced into

$$X_1' = F_1\left(X_1, M_2^{-1}(\xi - M_1X_1)\right). \tag{17}$$

- Grand Canonical System.
  By treating $X_2 = X_2^0$ as a constant vector, equation (16) is reduced into

$$X_1' = F_1(X_1; X_2^0). \tag{18}$$

Canonical System and Grand Canonical System

- (Gibb's Principle) For given X_2^0 and ξ, let X_c^* and X_{gc}^* be the equilibrium points of systems (17) and (18), respectively. If $X_2^0 = M_2^{-1}(\xi - M_1 X_c^*)$, then $X_c^* = X_{gc}^*$.
- Systems (17) and (18) share the "same" Lyapuov functions.
- Both X_c^* and X_{gc}^* are all asymptotically stable nodes.

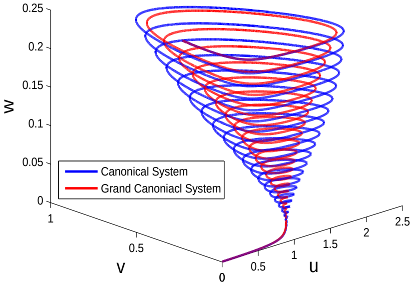
Recall
$$\begin{cases} \frac{du}{d\tau} &= u(w-v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} &= v(u-1) - \varepsilon v^2 + \varepsilon z \\ \frac{dw}{d\tau} &= -\sigma(wu - \varepsilon\sigma u^2) \\ \frac{dz}{d\tau} &= v - \varepsilon z. \end{cases} \tag{19}$$

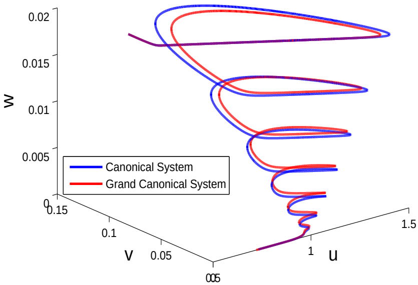
Canonical
$$\begin{cases} \frac{du}{d\tau} &= u(w-v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} &= v(u-1) - \varepsilon v^2 + \varepsilon\left(\xi - u - v - \frac{w}{\sigma}\right) \\ \frac{dw}{d\tau} &= -\sigma(wu - \varepsilon\sigma u^2) \end{cases} \tag{20}$$

Grand Canonical
$$\begin{cases} \frac{du}{d\tau} &= u(w-v) - \varepsilon(\sigma u^2 - v^2) \\ \frac{dv}{d\tau} &= v(u-1) - \varepsilon v^2 + \varepsilon z \\ \frac{dw}{d\tau} &= -\sigma(wu - \varepsilon\sigma u^2) \end{cases} \tag{21}$$

Canonical System vs Grand Canonical System

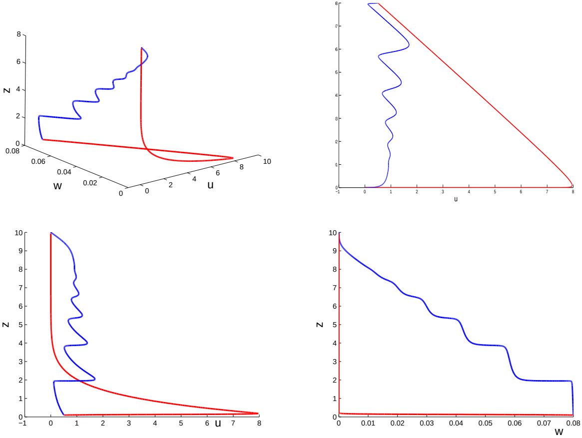
- System (20) admits similar dynamics as (21) does.





Canonical System vs Grand Canonical System

- When $v = v^* \sim \varepsilon$.



Future Work

- Effect of noise on the dynamics
  - Macroscopic level– Fokker-Planck equation
  - Microscopic level– chemical master equation(in progress)
- Dissipative perturbation of conserved system.

Thank you!